FORM PTO-1390 (REV 11-98) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: 515-4195

U.S. APPLICATION NO. (If known, see 37 CFR 1.5): 09/530246

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP98/06804	27 October 1998	28 October 1997

TITLE OF INVENTION: PROCESS AND PLANT TO EXTRACT AND CONCENTRATE TANNINS FROM WOOD AND FROM OTHER NATURAL PRODUCTS

APPLICANT(S) FOR DO/EO/US: Carlo MUSTACCHI; Giacomo MATTURRO; Paolo DANESI; and Andrea FESTUCCIA

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [ ] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [X] Other items or information:

Search report and cited documents;
Report of International Preliminary Examination Authority;
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PRINTED NAME: JAMES V. COSTIGAN

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U.S. APPLICATION NO. (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/530246	PCT/EP98/06804	515-4195

17. [X] The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

	CALCULATIONS PTO USE ONLY
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$970.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$840.00**	
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International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$670.00**	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$96.00**	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 840.00
Surcharge of **$130.00** for furnishing the oath or declaration later than [0] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 0

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	23 - 20 =	3	X **$18.00**	$ 64.00
Independent claims	3 - 3 =	0	X **$78.00**	$ 0
MULTIPLE DEPENDENT CLAIM(S) (if applicable)		0	+ **$260.00**	$ 0
TOTAL OF ABOVE CALCULATIONS =				$ 904.00
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also by filed (Note 37 CFR 1.9, 1.27, 1.28).				$ 452.00
SUBTOTAL =				$ 452.00
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$
TOTAL NATIONAL FEE =				$ 452.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00
TOTAL FEES ENCLOSED =				$ 492.00
				Amount to be: refunded $
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a. [X] A check in the amount of $ 492.00 to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 08-1540. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:
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212-302-8989

SIGNATURE:
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25,669
REGISTRATION NUMBER

Applicant or Patentee: Carlo MUSTACCHI(deceased) heir: Adriana ARCANGELI, Giacomo MATTURRO, Paolo DANESI and Andrea FESTUCCIA

Attorney's Docket No.: 515-4195 1313PT USA

Serial or Patent No.: NOT YET ASSIGNED

Filed or Issued: Concurrently Herewith

For: PROCESS AND PLANT TO EXTRACT AND CONCENTRATE TANNINS FROM WOOD AND FROM OTHER NATURAL PRODUCTS

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) and 1.27(c)) — SMALL BUSINESS CONCERN

I hereby declare that I am

( ) the owner of the small business concern identified below:
(X) an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN PRORAS S.r.l.

ADDRESS OF CONCERN Via Brenta 2/A - 00198 ROMA - ITALY

I hereby declare that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled PROCESS AND PLANT TO EXTRACT AND CONCENTRATE TANNINS FROM WOOD AND FROM ... by inventor(s) Carlo MUSTACCHI (deseaced) heir: Adriana ARCANGELI, Giacomo MATTURRO, Paolo DANESI and Andrea FESTUCCIA described in

(X) the specification filed herewith
( ) application serial no. _____, filed _____.
( ) patent no. _____, issued _____.

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(d) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e). *NOTE: Separate verified statements are required from each person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

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I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Vincenzo SANTONI

TITLE OF PERSON OTHER THAN OWNER Sole Director

ADDRESS OF PERSON SIGNING Via Brenta 2/A - 00198 ROME - ITALY

SIGNATURE X Vincenzo Santoni DATE 14 April 2000

Docket No.: 515-4195

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PATENT OPERATION

In re Application of:

Carlo MUSTACCHI
Giacomo MATTURRO
Paolo DANESI
Andrea FESTUCCIA

Group Art Unit: --

Examiner: --

Serial No.: Not Yet Assigned

Filed: Concurrently Herewith

For: **PROCESS AND PLANT TO EXTRACT AND CONCENTRATE TANNINS FROM WOOD AND FROM OTHER NATURAL PRODUCTS**

New York, NY 10036
April 26, 2000

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

PRELIMINARY AMENDMENT

SIR:

Prior to calculating the filing fee, kindly enter the subject amendment:

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James V. Costigan, Registration No. 25,669
(Typed or printed name of person mailing)

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IN THE CLAIMS:

Kindly amend claims 3-7, 9-12, 14-15, 18-20 and 22 under the provisions of 37 CFR 1.121(b) by deleting the bracketed subject matter and inserting the underlined material:

3. (amended) Process according to claim[s] 1[-2] wherein the membranes have spiral wound modules with spacing in the range 30-120 mil.

4. (amended) Process according to claim[s] 1[-2] wherein the membranes have spiral wound modules with spacing in the range 30-90 mil.

5. (amended) Process according to claim[s] 1[-2] wherein the membranes have spiral wound modules with spacing in the range 40-50 mil.

6. (amended) Process according to claim[s] 1[-5] wherein the extraction is carried out with water at temperature 90° - 115°C and at pressure P=0-3 10^{-1}MPa, the pH of water being comprised between 1,5 and 6 and an efficaceous mutual movement between the solid and the solvent being provided.

7. (amended) Process according to claim[s] 1[-6] wherein the extraction is carried out in a closed cycle with at least one extractor, the tannin solution being collected at the bottom of the extractor and being recycled, at least once, to the tope of the extractor or, in case of more than one extractor, to the top of the next extractor.

9. (amended) Process according to claim[s] 1[-8] wherein the percolation solvent flows parallel to the main axis of the extractor, going in contact with the solid material with water and/or steam jets directed from

top to bottom and/or from bottom to tope of the extractor.

10. (amended) Process, according to [any of the claim[s] 1[-9] wherein the length of the extraction cycle is 3-4 hours.

11. (amended) Process according to [any of the previous claims] claim 1 wherein the solvent is sent to the solid [material] product in a turbulent manner.

12. (amended) Process according to [any of the previous claims] claim 1 further comprising: a flotation/sedimentation stage, a filtration stage, a possible intermediate storage, from which the tannin solution is drawn to be nanofiltered at least once.

14. (amended) Process according to [the previous claims] claims 1 wherein the nanofiltration is carried out at P = 3.5 - 4.0 MPa and T + 50 - 70°C.

15. Process according to [the previous claims] claim 1 wherein the water outgoing the nanofiltration step is recycled as solvent to the extraction unit.

18. (amended) Plant according to claim [17] 16 wherein the nanofiltration unit comprises at least one spiral wound membrane with 30-120 mil spacing.

19. (amended) Plant according to claim[s] 16 [-18] wherein the extractor is a cylindrical vessel with the bottom in the shape of frustum of cone, on top of said extractor being positioned a charging hopper and a valve; inside the extractor being positioned at least a device to move the solid; the water and/or the steam for percolation are sent to the solid material in a turbulent manner by a device provided with sprayers, possibly

cooperating at the bottom of the extractor with another spraying device, at said bottom an intake being further positioned that, connected to a circulation pump, allows to send the water/tannin solution from the bottom to the top of the same extractor or to the next one and a valve allowing to unload the exhausted solid when the extractor is emptied.

20. (amended) Plant according to [any of the] claim[s] 16[-19] wherein the extractor further comprises a vibration device.

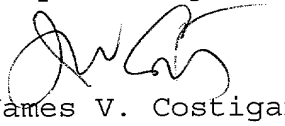
22. (amended) Plant according to [any of the] claim[s] 16[-21] further comprising, in relation of cooperation: a flotation/sedimentation unit, a filtration unit and possibly an intermediate storage unit from which the tannin solution is drawn to be sent to the nanofiltration unit.

Kindly cancel claims 24-27.

REMARKS

This Preliminary Amendment is being filed to reduce the filing fee.

Respectfully submitted,



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PROCESS AND PLANT TO EXTRACT AND CONCENTRATE TANNINS FROM WOOD AND FROM OTHER NATURAL PRODUCTS

Field of the invention

The present invention refers to a process and a plant to extract and concentrate tannins from wood and from other solid natural products containing it.

Background art

In the present description the word tannin(s) identifies a class of products, the vegetable tannins, comprising natural products contained in several parts of trees and plants (leaves, fruits, barks, wood and roots).Tannins are a complex of organic compounds and it is difficult to characterise their various components, in any case the tannins to which the present invention refers can be defined as a mixture of polyphenols with molecular weights ranging between 500 and 3000 dalton and can be subdivided into two sub-groups: hydrolyzable tannins and condensed tannins (Kirk-Othmer "Encyclopedia of Chemical Technology" 2nd Ed. vol. 12, 319-324).

Even though the above mentioned tannins can be used as mordant agents for dyes, in the production of inks, in the oenologic and pharmaceutical fields, their primary use is in the tannage industry. In fact the most important feature of tannins is that they combine with collagen and other proteic substances contained in the animal skin, thus transforming it into leather. For such uses it is important that in the tannin extracts, the hydrolyzable tannins be present in very low amounts, preferably as impurities. Therefore the present invention is focused to obtain highly concentrated condensed tannin solutions.

The main sources of such tannins are: chestnut wood, quebracho wood, sumach leaves, wood and bark of some kinds of oaks, myrobalan.

The extraction process of tannins from vegetal products containing them is a traditional method and it is based on extraction with boiling water. The thus obtained solution is concentrated by evaporation. This method is known since the beginning of this century and substantially nothing has been modified, except for the traditional boiling pools, that have been replaced with counter-current extractors, which, in any case, do not allow higher extraction yields, in that the

final tannin solution is still scarcely concentrated (about 5% by weight).

According to known techniques, as described in M. Giua "Trattato di Chimica Industriale" UTET, 45-49 (1973), chopped wood is loaded into a battery of autoclaves working in counter-current. In this manner fresh water meets the exhausted wood and the outgoing solution, enriched in tannin, solubilizes the tannin contained in high concentration in the fresh chopped wood incoming the battery of autoclaves. This treatment, called leaching, is carried out generally in water at about 110 - 120°C and at a maximum pressure of (0.8 bar) 0.810^{-1} MPa for about 6 hours, with a water/wood ratio of about 2 - 2.4 by weight. Generally, through this boiling treatment a tannin solution at 4 - 5% by weight is obtained, with an extraction yield of about 60 - 65% (R. Jullien, Durand Ayme "Le tannnage vegetal", Centre technique de cuir Ed., (1980). After clarification by settling, the tannin solution is concentrated in multiple evaporators, under vacuum to limit the tannin oxidation, up to the desired concentration (generally 40 - 50% by weight). The thus obtained solution can be added up with known stabilising agents and stored, or it can be further treated, for example it can be powder dried, for example atomised.

The main drawbacks, that make unacceptable the above process, are the following: low extraction yields, too large amounts of water to be used, too high energy consumption to evaporate such water.

Several plants are known to perform the tannin extraction, however their main drawback is that the contact between the extraction fluid and the material to be extracted is unsatisfactory, thus making poor the plant performances.

The use of filtration membranes is known in this field, however the products obtained till now are unsatisfactory, both in terms of quality of the final product and/or in terms of the performances of the membranes.

The present invention solves the above problems.

Summary of the invention

It is an object of the present invention to provide a method to extract tannins from vegetal products and to concentrate the thus obtained tannin solution, the extraction being carried out by percolation and the concentration being carried out

by nanofiltration with spiral wound membranes.

Another object of the invention is to provide a plant to extract and concentrate the tannin solution, said plant comprising at least an extractor and a nanofiltration stage.

A further object of the invention is the use of nanofiltration spiral wound membranes to concentrate the tannin aqueous solution up to the desired value.

Other objects will be evident from the detailed description of the invention.

Brief description of the drawings

Fig.1 is a block diagram of a preferred process according to the invention.

Detailed description of the invention

In the present description, the word "nanofiltration" is referred to filtration techniques carried out by membranes; the wordings "ultrafiltration" and "reverse osmosis" are here both synonym of the word "nanofiltration". These techniques allow to separate different kinds of molecules present in a solution; they are based both on a mechanical separation and on a chemical-physical separation, the last one relating to the different chemical and physical affinity of the molecules to be separated with respect to the nature of the membranes.

The method described in the present invention is based on the fact that the solid material to be extracted, chopped by traditional techniques, is subjected to an extraction by percolation with water and the thus obtained aqueous solution is nanofiltered with suitably selected membranes, that allow to obtain tannin concentration of 50% by weight in tannin or higher.

It must be stressed that the percolation technique requires plant structures more complex and more expensive than the counter-current ones, however, according to tests performed by the applicants, not only the initial high investment costs turn into a final saving, but also the so obtained product is better than the one obtained in the traditional way, as shown below.

The extraction by percolation according to the invention is carried out by an extraction unit 1, comprising at least an extractor, wherein a water flow, preferably demineralized water, and/or a steam flow, comes in contact with the solid material to be extracted. The water has a temperature ranging between 90° and 115°C and

it is acid (pH= 1.5-6) to increase the extraction power; pressure is maintained between (0 and 3 bar) 0 and 3 10^{-1} MPa. Water extracts tannin from the solid material and the resulting solution is collected at the bottom of the extractor. Preferably this extraction stage is carried out in a closed cycle, that is, the tannin solution at the bottom of the extractor is recycled, at least once, preferably, from 6 to 10 times per hour to the top of the extractor or, in case of more than one extractor, to the top of the next extractor.

The extractor is a vessel of variable capacity in accordance with the plant capacity, generally built in stainless steel (AISI 304), cylindrical in shape and with the bottom in the shape of frustum of cone. On top of the extractor there are positioned a charging hopper and a valve to guarantee the seal. A device fit to move the solid bed of material, for example an Archimedean screw, can be positioned inside the extractor. The water and/or the steam for percolation are sent to the solid material in a turbulent manner, in order to increase the extraction yield. To this purpose, at least two ring shaped pipes are positioned on top and inside the extractor, such pipes being provided with sprayers to pour fresh solvent, possibly cooperating with at least another ring of sprayers at the bottom of the extractor. At the bottom it is also positioned an intake that, connected to a circulation pump, allows to send again the water/tannin solution from the bottom to the top of the extractor, in order to increase the power of extraction. On a flange at the bottom of said extractor a valve is positioned to allow the unloading of the exhausted solid, after the extractor is emptied.

In order to further increase the extraction yield, a vibration device can be provided, preferably placed at the bottom of the extractor. An electromechanical vibrator such as a piezoelectric transducer can be used. Such device increase the mutual movement between the material to be extracted and the extraction fluid.

According to a preferred embodiment, the flow of the percolation solvent goes parallel to the main axis of the extractors so that said solvent goes in contact with the solid in water and/or steam jets directed from top to bottom and/or from bottom to top, thus increasing the contact time of the water with the solid. The operative conditions of the extractor 1 are preferably the following: T = 90 - 110°C, pH = 4 -

6, P = (0 - 1 bar) 0 - 1 10^{-1} MPa, duration of the extraction cycle: 3 - 4 hours.

The extraction stage, carried out according to the invention, allows to obtain an extraction yield of 90 - 95%. The tannin solution coming from the extraction unit 1 is sent to the flotation/sedimentation unit 2 that works in a known way. Such unit 2 comprises an atmosphere basin where the solution settles and all the floating parts are eliminated with a skimmer and all the thickened muds at the bottom are eliminated with a scraper. Afterwards the solution is sent to the filtration unit 3, known *per se*, in order to eliminate the residual deposits. Preferably the filtration is carried out with filters, for example basket filters, leaf-filters or other kind of well-known filters, to stop particles up to 10 μm. After this unit 3, an intermediate storage unit 4 could be provided, from which the solution is drawn to be nanofiltered in the next stage 5.

The nanofiltration is carried out by membranes that, performing a specific mechanical action and having a chemical-physical affinity to tannin, concentrate the entering tannin solution and let the water without tannin to go out. This water is recycled in the plant, after proper treatment, as described below.

The tannin solutions outgoing the membranes are highly concentrated, more than 50% by weight in tannin and can be used as such for tanning operations.

It has been found that the best membranes to be used are the nanofiltration membranes with spiral modules. In fact it has been found that, owing to the complexity of the product to be separated (the polyphenols mixture called tannin), membranes with different configurations do not guarantee adequate performances in terms of life. Also the spacing has been found to be a parameter having influence on the efficiency of the nanofiltration and suitable spacing has been found to be in the range 30-120 mil, preferred range 30-90 mil, particularly preferred range 40-50 mil, "mil" being a measure known to the experts in this field.

Preferred operative conditions are: P = (35 - 40 bar) 3,5 - 4 MPa, T = 50 - 70°C.

Preferred membranes are pressure driven membranes with 200-500g/mole molecular cut off. The polysulphone membranes and polyamide membranes are particularly preferred.

The concentrated solution outgoing from the membranes is typically about 50% by

weight in tannin or higher, with pH=3 - 3.5, and the permeated water has a pH = 5 - 5.5. The above described nanofiltration process permits to extract more than 95% tannins from the solution.

There can be more than one nanofiltration stages, as the case requires. It is possible to put a plurality of membranes, connected in series. Moreover, to further increase the extraction yields, a vibration device can be provided, in combination with the spiral wound membranes. An electromechanical vibrator such as a piezoelectric transducer can be used, which can be advantageously placed in the housing of the membrane.

The substantially free of tannins water outgoing the membranes is recycled as solvent to the extraction unit 1, being previously subjected to known treatments, such as a neutralisation.

The plant can be supplied with a storage unit 7 for water. The final tannin solution is collected in a storage unit 6 in order to be sent to a packing unit or to other post-treatments, such as drying process (drawer filters, drum filters, atomisation) to obtain tannin powder.

An advantage of the process of the invention comes from the fact that tannin produced in this way, not being subjected to heavy heat - treatments (except the first one in the extraction stage, that in any case is less heavy than the traditional one), is not so degraded (oxidated) as the products obtained with traditional methods; therefore it has higher activity, for example in terms of tannage power, than the corresponding traditional ones. Another advantage is that the tannin solution outgoing the membranes can be directly used for tanning and further concentration steps are not necessary in that tannin solutions having concentrations of about 50% by weight in tannin are suitable for tanning.

Other advantages of the process and the plant described in the invention are found in the economic and ecological fields. The ecological advantages come from the fact that the volumes of wasted water in the innovative plant are 4 times lower than in the traditional ones. Besides, there is no need to evaporate huge quantities of water and the amount of fuel used is enormously lower than the corresponding one used in the traditional technologies. Moreover, by the

nanofiltration there are no possibilities for the tannin to be dragged in the atmosphere together with the evaporated water.

The economic advantages are related to the running costs of the plant, that can be cut down to one third of the traditional plant costs, thanks to the low amounts of fuel needed and thanks to the lower investment costs of mechanical concentrators by nanofiltration with respect to the traditional evaporators.

The following examples are intended to illustrate the invention and they should not be considered to limit the invention itself.

EXAMPLE 1

Extraction

The extraction unit comprised three extractors connected in parallel; each extractors of 2000 litres capacity. The load was 350 kg of chopped chestnut wood to each extractors.

Extraction temperature: 110°C

Pressure: P = (0.8 bar) 0.8 10^{-1} MPa

Number of recycles: 10 per hour

Duration of the extraction cycle: 4 hours

water/wood ratio: 1:1 by weight

The outgoing product at the end of the treatment had a tannin concentration of 8% by weight, with an extraction yield of 95%.

EXAMPLE 2

Concentration by nanofiltration.

To run this test the following membranes, produced by Hoechst Separation Products were used, having the following characteristics:

polyetherosulfonic NF PES10 10H® spiral wound 4" x 40", 44 mil

polyetherosulfonic N 30 F® spiral wound 4" x 40", 44 mil

polyamide Desal 5 DK® spiral wound 4" x 40", 50 mil

The solution coming from the extraction unit, after proper clarification, was subjected to nanofiltration according to the operative conditions listed in Table 1. The results are shown in Table 1, pH of the permeated solution pH = 5.5.

Table 1

membrane	temperature °C	pressure MPa	permeate concentration[a]	permeate flux[b] l/m²h	rejection[c] %
NF PES10 10H®	40	3	46.7	17.5	98.6
	50	4	53	22	98.9
N 30 F®	40	3	43.3	16.1	98.4
	50	4	49.7	18.3	98.6
Desal 5 DK®	40	3	51.1	20	99.6
	50	4	58.7	25	99.8

[a] *tannin concentration outgoing the membrane (% b.w.)*

[b] *unitary flow of tannin solution passing through the membrane*

[c] *tannin amount extracted from the starting tannin solution*

Backwashings of the membranes with NaOH-water solutions did not show problems and the membranes were quickly regenerated, with no damages for them. The original fluxes of the modules were reproducible after cleaning procedures.

EXAMPLE 3 (comparative example)

The concentration was carried out as described in Example 1, but the spiral wound membranes were replaced by a polyamide tubular membrane AFC99, produced by PCI Membrane Systems Ltd. The average permeation rate (permeate flux) was 5 l/m²h. The concentration of the tannin solution outgoing the membrane was 18.3% b.w..

The further backwashing of the membrane became soon difficult and after a six weeks operative life, the membrane was no more usable.

From Examples 2 and 3 it is evident that only spiral wound membranes can be suitable for the tannins extraction. Different membranes give final solutions characterised by low tannin amounts, moreover the permeate flux is unsatisfactory.

Inside the group of the spiral wound membranes the experts in this field will find the best operative conditions. Applicant has found that Desal 5 DK® 50 mil had the

best performances.

Tanning tests, performed by using the tannin solutions obtained according to Example 2 and corresponding commercial products, show much better results for the tannins of the invention in terms of tanning yield and touch of the leather.

CLAIMS

1. Process to extract and concentrate tannin from solid natural products containing it, said process comprising the steps of subjecting the solid products to an extraction by percolation with water and/or steam as solvent and concentrating the thus obtained tannin solution by nanofiltration with spiral wound membranes, said membranes being selected among the polyetherosulfonic or polyamidic ones.
2. Process according to claim 1 wherein the membranes are selected among polyetherosulfonic NF PES10 10H® spiral wound membrane, polyetherosulfonic N 30 F® spiral wound membrane, polyamide Desal 5 DK® spiral wound membrane.
3. Process according to claims 1-2 wherein the membranes have spiral wound modules with spacing in the range 30-120 mil.
4. Process according to claims 1-2 wherein the membranes have spiral wound modules with spacing in the range 30-90 mil.
5. Process according to claims 1-2 wherein the membranes have spiral wound modules with spacing in the range 40-50 mil.
6. Process according to claims 1-5 wherein the extraction is carried out with water at temperature 90° - 115°C and at pressure P = 0 - 3 10^{-1} MPa, the pH of water being comprised between 1,5 and 6 and an efficaceous mutual movement between the solid and the solvent being provided.
7. Process according to claims 1-6 wherein the extraction is carried out in a closed cycle with at least one extractor, the tannin solution being collected at the bottom of the extractor and being recycled, at least once, to the top of the extractor or, in case of more than one extractor, to the top of the next extractor.
8. Process according to claim 7 wherein the tannin solution is recycled from 6 to 10 times per hour.
9. Process according to claims 1-8 wherein the percolation solvent flows parallel to the main axis of the extractor, going in contact with the solid material with water and/or steam jets directed from top to bottom and/or from bottom to top of the extractor.
10. Process, according to any of the claims 1-9 wherein the length of the extraction

cycle is 3 - 4 hours.

11. Process according to any of the previous claims wherein the solvent is sent to the solid material in a turbulent manner.

12. Process according to any of the previous claims further comprising: a flotation/sedimentation stage, a filtration stage, a possible intermediate storage, from which the tannin solution is drawn to be nanofiltered at least once.

13. Process according to claim 12 wherein the filtration is carried out by basket and/or leaf filters.

14. Process according to the previous claims wherein the nanofiltration is carried out at P = 3.5 - 4.0 MPa and T = 50 - 70 °C.

15. Process according to the previous claims wherein the water outgoing the nanofiltration step is recycled as solvent to the extraction unit.

16. Plant to extract and concentrate tannin from natural solid products containing it, characterised by comprising an extraction unit (1) in which the solid material is subjected to an extraction by percolation with water and/or steam as solvent and a nanofiltration unit operating with spiral wound membranes, said membranes being selected among the polyetherosulfonic or polyamidic ones.

17. Plant according to claim 16 wherein the membranes are selected among polyetherosulfonic NF PES10 10H® spiral wound membrane, polyetherosulfonic N 30 F® spiral wound membrane, polyamide Desal 5 DK® spiral wound membrane.

18. Plant according to claim 17 wherein the nanofiltration unit comprises at least one spiral wound membrane with 30-120 mil spacing.

19. Plant according to claims 16-18 wherein the extractor is a cylindrical vessel with the bottom in the shape of frustum of cone, on top of said extractor being positioned a charging hopper and a valve; inside the extractor being positioned at least a device to move the solid; the water and/or the steam for percolation are sent to the solid material in a turbulent manner by a device provided with sprayers, possibly cooperating at the bottom of the extractor with another spraying device, at said bottom an intake being further positioned that, connected to a circulation pump, allows to send the water/tannin solution from the bottom to the top of the same extractor or to the next one and a valve

allowing to unload the exhausted solid when the extractor is emptied.

20. Plant according to any of the claims 16-19 wherein the extractor further comprises a vibration device.

21. Plant according to claims 20 wherein the vibration device is a piezoelectric transducer.

22. Plant according to any of the claims 16-21 further comprising, in relation of co-operation: a flotation/sedimentation unit, a filtration unit and possibly an intermediate storage unit from which the tannin solution is drawn to be sent to the nanofiltration unit.

23. Plant according to claim 22 in which the filtration unit comprises basket and/or leaf filters.

24. Use of polyetherosulfonic or polyamidic spiral wound membranes in the nanofiltration technique to concentrate condensed tannin solutions.

25. Use of polyetherosulfonic NF PES10 10H® spiral wound membrane in the nanofiltration technique to concentrate condensed tannin solution.

26. Use of polyetherosulfonic N 30 F® spiral wound membrane in the nanofiltration technique to concentrate condensed tannin solution.

27. Use of polyamide Desal 5 DK® spiral wound membrane in the nanofiltration technique to concentrate condensed tannin solution.

AMENDED SHEET

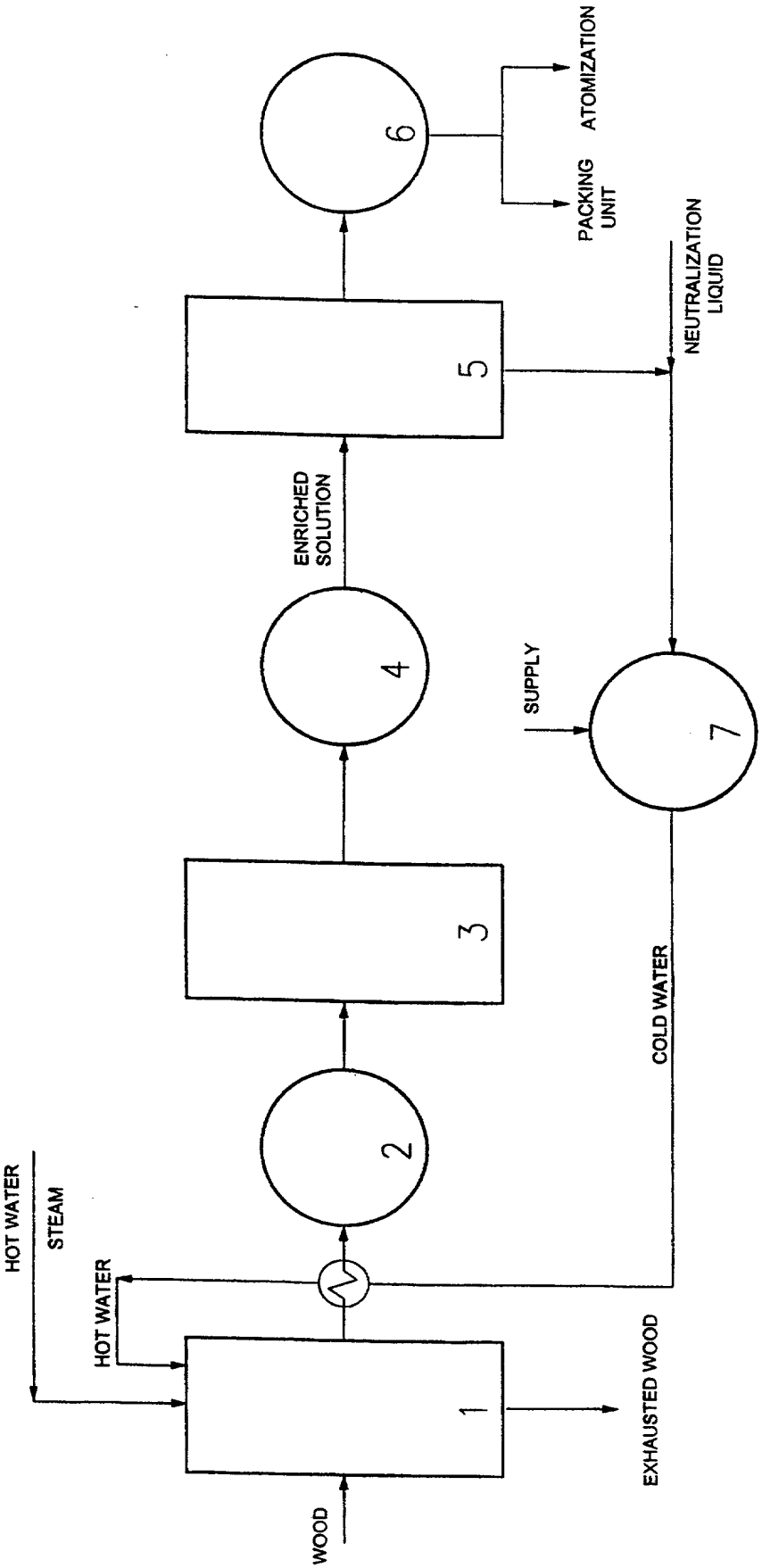
WOOD
HOT WATER
STEAM
HOT WATER
1
2
3
4
5
6
7
EXHAUSTED WOOD
COLD WATER
ENRICHED SOLUTION
SUPPLY
NEUTRALIZATION LIQUID
PACKING UNIT
ATOMIZATION

FIG.1

Docket No: 515-4195

APPLICATION FOR UNITED STATES LETTERS PATENT
DECLARATION, POWER OF ATTORNEY, AND PETITION

As a below-named inventor, I declare that:

My residence, post office address and citizenship are as stated next to my name; I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the invention which is described and which is claimed in the specification, entitled: PROCESS AND PLANT TO EXTRACT AND CONCENTRATE TANNINS FROM WOOD AND FROM OTHER NATURAL PRODUCTS

The specification [X] is attached hereto [ ] was filed on _____, as Application Serial No. _____.

☒ was filed as PCT international application
Number PCT/EP98/06804
on 27 October 1998
and was amended under PCT Article 19
on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of said specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.[1]

COUNTRY	APPLICATION NUMBER	DATE (Day, Month, Year)	PRIORITY CLAIMED UNDER 35 U.S.C. 119
ITALY	RM97A000653	28 October 1997	Yes [X] No [ ]
			Yes [ ] No [ ]

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

[1] In Non-Convention cases, a listing of all filings and current status of cases filed more than a year before the U.S. filing is required to comply with 37 CFR 1.56(a). Such a listing may be attached.

1313 PT
USA

APPLICATION SERIAL NO.	FILING DATE	STATUS

I hereby appoint my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the U.S. Patent & Trademark Office connected therewith:

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The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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